

A STUDY OF THE STRUCTURE, INTERFACIAL
REACTIONS, AND RECTIFYING PROPERTIES
OF SELENIUM FILMS

BY
PAUL GORDAN ROACH
B.S., Indiana University, 1936

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1940

URBANA, ILLINOIS
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Since the discovery by Adams and Day¹ that there was a difference in resistance in two electric current directions in a selenium cell, many investigators have worked with cells of this type with the purpose of constructing an apparatus which could be used as a dry plate rectifier. From the results on these independent researches the information was obtained that, with ordinary light sensitive selenium cells, the difference in resistance in two current directions could be increased if one of the electrodes touched the selenium lightly or if the electrodes were made of different materials. With this information at hand, Presser² succeeded, after a great deal of experimentation, in constructing a suitable rectifier. For one of the electrodes he used a metal from the iron group of elements and for the other some alloy of lead or bismuth.

Although many patents have been issued on this type of rectifier, there is no detailed information in the literature concerning the influence of the many factors involved. The principal conclusion gained from publications is that selenium films formed by one means or another must be subjected to heat treatments at various temperatures for varying lengths of time to convert them into the proper form for effective rectifying action. Certain addition agents have been recommended, but the claims for their influence have not been consistent.

Several theories have been advanced to explain the rectifier action of both selenium and other kinds of dry rectifiers. Reichinstein³ has summed up the earlier theories and said that rectification may be explained by (1) a high polarization potential; (2) an unsymmetrical Becquerel effect; and (3) the occurrence of polarization at discontinuities in the interior of the solid material. Later Eccles⁴ and Owen⁵ carried out experiments which tended to prove that rectification was caused by thermal effects. Barnard⁶ disputed this and proposed a theory based on a lattice loosening brought about by a concentration of electric energy about the 'point' of contact of one of the electrodes. Schottky⁷ proposed a "blocking layer" consisting of a high resistance material at one of the rectifier layer interfaces and Wilson⁸ proposed a theory which involved the necessity for such a "blocking layer." His theory was based

on the difference in electron energy bands in the semiconductor and metallic electrode and assumed a transfer of electrons from the metal to the semiconductor by the "tunnel effect" through the barrier layer. Mott⁹ recently has disputed this theory and proposed one which requires that the electrons be thermally excited over the barrier rather than through it.

Because X-ray methods have been very useful in studying problems which defied solution by many other methods, they were adopted in the present work for the investigation of changes which take place in selenium films when subjected to different treatments and conditions.

Again, because information in the literature is fragmentary as to the exact methods for and conditions of formation of these films and their subsequent treatments, it was desirable to carry out investigations along these lines. The various problems which have been studied include the techniques and materials necessary for the construction of rectifiers and subsequent measurement of their resistance in two current directions, the influence of heat treatments on crystal structure and rectifying properties, the influence of substances probably formed at the different interfaces in a rectifier sample, the effects of addition agents and impurities in the selenium, studies on polarization, heat treatments in different atmospheres and polishing the selenium surfaces, and the effects of crystalline layers formed by organic reagents.

SUMMARY OF RESULTS

1. A description has been given of the apparatus used for measuring the resistances of rectifier samples. It was found necessary to use samples in the form of a flat plate to satisfy the requirements for ease of formation of selenium films, making resistance measurements, and studying the films by X-ray methods. Methods for preparation of the backing electrodes, casting selenium films, and attachment of the counter electrode have been discussed.

2. Results from experiments on heat treating of selenium films showed that at temperatures between 100°C and 120° the selenium was changed from the amorphous to the hexagonal crystalline form. The electrical resistances of films formed at this temperature were great and rectifying properties were not exhibited. Heating at temperatures near 200°C caused a rapid decrease in electrical resistances, the exhibition of rectifying action, and an increase in crystal size. Crystal size, how-

ever, was not always a direct measure of the resistances.

3. It has been shown that the ultimate resistance of a selenium film cast onto an iron or nickel backing electrode is influenced by the temperature to which the electrode is heated and the time of exposure to air during heating before molten selenium is applied. This influence was attributed to oxides which formed on the backing electrode surfaces.

4. It was not possible to detect the presence of selenides at interfaces of rectifying layers by X-ray methods, but certain colorations at these interfaces indicated that they were formed. The electron diffraction method is evidently required to detect these very thin films.

5. Results were obtained which showed that there was not a high resistance layer at the selenium-backing electrode interface.

6. From the results on experiments involving the addition of certain substances to selenium, purification of commercial selenium, spectrographic studies, and interchange of selenium and backing electrodes from commercial rectifiers and rectifiers constructed during the present investigation, the conclusion was reached that impurities present in very small amounts were not very influential on the ultimate resistances and rectifying properties of selenium films. Materials added to selenium in concentrations from 0.1 to 5% increased resistances and did not improve rectification.

7. By measurements of change of resistance with time of flow of current on commercial rectifiers and rectifiers prepared during the present investigation, it was found that polarization took place. Wilson's⁸ theory of the potential barrier function was qualitatively satisfied in most instances.

8. Evidence obtained from heat treatments in different atmospheres, polishing of selenium film surfaces, crystallization of amorphous selenium by organic reagents, and other experiments showed that the rectifying contact of a selenium rectifier is at the selenium-counter electrode interface.

9. X-ray studies of polished and unpolished surfaces indicated a decrease in crystal size during polishing. A very thin film of crystalline selenium did not change except for an increase in crystal size when heated at 208°C for 3 hours. This disproved Gripenberg's¹⁰ contention that an amorphous layer resulted.

10. A discussion has been presented to show how a polished layer,

if it were composed of finely divided crystals, could have a high electrical resistance.

11. Experiments with phenylhydrazine and quinoline showed that these two reagents change amorphous selenium to the hexagonal form. Phenylhydrazine gave rise to crystalline films in which crystals had a preferred orientation while quinoline produced films in which crystals were nearly randomly oriented. A mechanism has been proposed which could account for this difference.

12. It was shown that crystalline selenium layers formed by quinoline enhanced rectifying properties and that those formed by phenylhydrazine inhibited these properties. From data on orientation this led to the conclusion that selenium crystals do not conduct electricity as well in the direction of the major axis as along other crystal directions.

13. Data were not sufficient to explain why some organic reagents change amorphous selenium to the monoclinic form while others cause a transformation into the hexagonal form. It was not possible to convert monoclinic selenium, formed by the action of ethyl alcohol on amorphous selenium, into the hexagonal form by use of phenylhydrazine.

14. A discussion has been presented of Mott's⁹ objection to Wilson's⁸ theory of contact rectifiers in terms of results obtained in the present investigation.

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VITA

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